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INVESTIGATION OF

LIQUID ROCKET PROPELLANTS

Contract N7onr-462
Task Order III
Project NR 220 023

Written by:
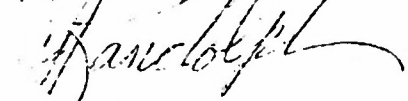
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Period Covered:

1 March through 31 May 1953

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CONTENTS

CONTENTS (cont.)

CONTRACT FULFILLMENT STATEMENT

This quarterly report is submitted in partial fulfillment of Contract N7onr-462, Task Order III, and covers the work done from 1 March through 31 May 1953.

I.   INTRODUCTION

Four investigations related to the development of improved rocket propellants were conducted during this quarterly report period. The study of the kinetics of the thermal decomposition of nitromethane was concerned primarily with the effect of added nitric oxide and hydrogen cyanide on the rate and course of the reaction at high pressure. The synthesis of N-aminoethylenimine was studied further, and a number of important physical properties of the material were determined. The first steps in a proposed synthesis of the as yet unknown compound N,N,N'-trimethyltriazane were conducted. The determination of the sensitivity of methylacetylene to rapid adiabatic compression and to ejection through small orifices at high pressure drops was completed.

II. KINETIC STUDY OF THE THERMAL DECOMPOSITION OF NITROMETHANE

A.   INTRODUCTION

1.   During this report period the main objective of this study has been to determine the effect of additives such as nitric oxide, hydrogen cyanide, and carbon dioxide on the rate of thermal decomposition of nitromethane at relatively high pressures, and on the qualitative and quantitative distribution of the reaction products. Two additional objectives were to re-examine the dependence of the concentration of nitric oxide formed on the initial pressure of nitromethane and to check the correction factor to be applied to polarographic analyses of nitromethane. Both these points have been previously discussed (Reference 1).

2.   All the decomposition experiments carried out during this report period were conducted at a temperature of 355°C, at pressures ranging from 85 to 275 psia, and for 31 minutes duration.

B.   APPARENT ORDER OF THE REACTION

1.   The kinetic experiments were conducted by determining polarographically the amount of undecomposed nitromethane remaining within a sealed glass ampoule after heating for a given period of time at specified conditions of temperature and initial pressure. It was reported (Reference 1) that a correction factor of 4% had to be applied to all test results in order to account for the low values obtained when ampoules containing known amounts of nitromethane were analyzed. This somewhat high correction factor was reinvestigated and it was found that the mean error was actually much lower, only -0.9%, with a standard deviation of 0.5 for five tests. The higher value obtained previously was probably caused by the fact that the determination was carried out before the analytical method had been reduced to a routine procedure. The percentages decomposed and the rate constants for a 1.3-order

II Kinetic Study of the Thermal Decomposition
   of Nitromethane, B (cont.)

Report No. 717

reaction, reported in Reference 1, were recomputed using the new correction factor. These results, together with those from additional decomposition experiments at 355°C for 31 minutes, are summarized in Figure 1 and Table I. The results have been shifted somewhat numerically, but the conclusions drawn in the last report concerning the kinetics of the reaction remain valid.

     2.   For some time during this report period, poorly defined polarographic curves were obtained for nitromethane, which made quantitative determinations difficult. A piece of Tygon tubing was found to be responsible for the difficulty. The tubing, approximately 1 ft long, was attached to a glass siphon used for removing the supporting electrolyte (0.05M H_2SO_4 saturated with Hg_2SO_4) from its stock bottle. It is believed that the plasticizer in Tygon was slowly leached out and caused another wave to overlap the nitromethane wave. After elimination of the tubing, well-defined and reproducible curves were again obtained.

   C.   EFFECT OF ADDITIVES

     1.   Extent of Decomposition

         a.   It was reported previously (Reference 1) that the addition of 1% of nitric oxide to nitromethane did not affect its rate of decomposition. It has now been found that when approximately 20% nitric oxide is added a definite inhibitory effect occurs (Table II). In order to exclude the possibility that the addition of a large amount of gas might influence the rate of the reaction because of an "inert gas effect," an equally large amount of carbon dioxide was added to nitromethane. It was found that the presence of carbon dioxide did not affect the rate of reaction. It must be concluded, therefore, that the inhibitory action of nitric oxide is specific.

         b.   An attempt was made to determine the effect of added hydrogen cyanide on the rate of decomposition of nitromethane; however, no well-defined polarographic curve could be obtained, thus making a quantitative analysis impossible. It appears that either the large additional amount of hydrogen cyanide or the presence of new compounds, formed by the reaction of hydrogen cyanide with nitromethane or its decomposition products (Section C.2.6), has a pronounced effect on the polarographic behavior of nitromethane. Information obtainable from the mass-spectrometer analyses will be of aid in determining whether the additional time necessary to resolve this situation is warranted by the results to be achieved.

2.   Products of the Decomposition

a.   It was reported previously (Reference 1) that the addition of 1% nitric oxide (NO) to nitromethane did not appreciably affect the composition and distribution of the reaction products. The addition of 20% nitric oxide, however, caused measurable changes in the relative amounts of reaction products, and brought about the appearance of larger amounts of materials which previously had been observed only in trace amounts, if at all. Table III lists the results of the analyses of the three samples to which nitric oxide had been added; for comparison, normal 31-minute decomposition runs have been included. The data were recalculated to exclude nitric oxide and to include only materials volatile at -78°C. Several observations concerning these data are in order.

(1)   The concentration of methane has been greatly decreased by the addition of 20% nitric oxide. The reason that there is a measurable concentration of methane in sample 107 but not in samples 101 and 99 may be attributed to the separation of this sample into various fractions, which increases the precision of identification and measurement of small amounts of materials.

(2)   The relative concentrations of nitrogen and carbon monoxide have increased over those in samples to which no nitric oxide was added. The differences in the concentrations of these products are much larger than could be accounted for by experimental variations.

(3)   The relative concentration of carbon dioxide has been somewhat decreased by the addition of 20% nitric oxide; this effect is particularly noticeable in samples 101 and 99. It should be remarked here that there is some uncertainty associated with the analysis of nitrous oxide and carbon dioxide, as both have molecular weights of 44. The sum of these two materials can be established with reasonable correctness. However, the assignment of the relative amounts of carbon dioxide and nitrous oxide depends, in the case of these samples, exclusively on a small peak in the cracking pattern of carbon dioxide. The consistent inability to calculate the pattern of carbon dioxide and account for all of the mass 44 peak indicates that some nitrous oxide is surely present; the precision of the determination, however, depends largely on the judgment of the computer. The significance of these results will be discussed in Section D.

(4)   In addition to the changes described above, a remarkable increase has been noted in the peak heights of as yet unidentified materials which had previously been noted only in trace amounts (Reference 1). More than one substance is probably involved. The largest peak appears at mass 54 and a slightly smaller one at mass 70, with clusters of smaller peaks

surrounding the larger ones. Peaks have also been noted at masses 82 and 84. The unidentified substances responsible for these peaks do not have appreciable vapor pressures at -78°C, but are completely volatilized at -48 to -46°C. If the higher mass peaks were temporarily ignored, the group of peaks about mass 54 could be accounted for fairly satisfactorily by n-propionitrile. The presence of still other materials is indicated by the inability to account completely for some of the lower mass peaks, such as 43 and 45. When these substances, whose concentration appears to be increased by added nitric oxide, are identified, the information will contribute to a fuller understanding of the function of nitric oxide in the nitromethane decomposition.

      b.   Table IV gives the results of Run 103. Approximately 20% hydrogen cyanide was added to this sample, and a complete analysis was performed. For comparison, the results of Run 92 have been recalculated to exclude hydrogen cyanide, and are included in the table. As in the case of added nitric oxide, there are several unidentified materials present in this sample. It is interesting to note, however, that the peaks grouped about masses 54 and 70 are present only in very small amounts and do not differ noticeably from those observed in runs without additives. The unidentified materials in this case seem to have peaks centered about mass 30. There is also some evidence of the presence of ethylene, but this will have to be checked more carefully.

      c.   It was noted often that a portion of the mass 15 peak could not be assigned to methane, as the 16 peak was too small. This situation was at first attributed to the behavior of the instrument; it was noted, however, that the extraneous mass 15 peak appeared only in samples which contained only the materials volatile at -78°C, especially when relatively large amounts of carbon dioxide were present. The magnitude of the peak was such that it could not be explained by the formation of NH^+ by a recombination process in the mass spectrometer, and since the presence of free CH_3 in the samples appeared unlikely, the problem remained unsolved. After some experimentation, it was established that the extraneous peak could be explained on the basis of the resolution of the mass spectrometer. The actual masses contributing to the mass 16 peak in the samples are methane (16.044) and oxygen (16.000).[*] With a high-resolution mass spectrometer such as that used at Aerojet, it is possible to observe a doublet at mass 16 if both materials are present. For general analytical work, however, it is frequently desirable to sacrifice resolution in order to increase the sensitivity and scanning speed of the instrument. This can be accomplished in the Aerojet instrument by opening the adjustable collector slit. In this event the two members of the doublet are focused on the collector plate simultaneously, and the measured peak is the sum of the

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[*]Reference 2.

doublet peaks. If the slit is not sufficiently wide, or if the resolution is quite high, the two peaks making up the doublet will overlap only partially, and the measured peak will be less than their sum. This situation apparently occurred; even with the slit wide open it was impossible to obtain complete additivity of the CH_4-O doublet. The mass 15 peak therefore is not too large; it is rather that the mass 16 peak is too small. The concentrations of methane have been recalculated in all samples as a result of this discovery; however, the correction in every case is only a few tenths of a percent, and well within the experimental error.

D. MECHANISM

1. Introduction

A number of aspects of the mechanism of the thermal decomposition of nitromethane were considered in the previous report (Reference 1). In the following discussion some of these ideas will be expanded in the light of the data obtained subsequently. In order to facilitate reference to the section of mechanism in the last report, the same sequence of subject matter will be maintained.

2. Free-Radical Mechanism

a. Inhibition of a reaction by the addition of nitric oxide is usually considered evidence for the occurrence of free-radical reaction steps. The fact that the addition of approximately 20% of nitric oxide inhibits the decomposition of nitromethane by approximately 36% indicates strongly that free radicals are involved. In the case of nitromethane, the situation is more complex than for the usual addition experiments, as nitric oxide is an intermediate reaction product and both the amount produced during the reaction and the amount added must be considered. The fact that relatively large amounts of nitric oxide are necessary to inhibit the reaction, while usually much smaller amounts are sufficient, may be explained as follows: (1) The reaction may be only a one- or two-step chain, in which case nitric oxide would have to destroy many more radicals than in a long chain reaction, or (2) the radicals involved may be different from those associated previously with nitric oxide inhibition. In the latter case nitric oxide may be relatively inefficient in its inhibitory action on these radicals.

b. Cottrell (Reference 3) has proposed a mechanism which involves only a one-step radical reaction:
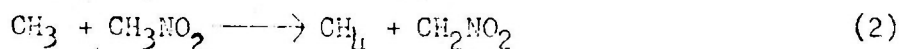
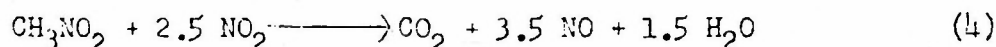$$CH_3NO_2 \longrightarrow CH_3 + NO_2 \tag{1}$$

$$CH_3 + CH_3NO_2 \longrightarrow CH_4 + CH_2NO_2 \tag{2}$$

The chain is not continued after this sequence. This would fit in with the low inhibitory efficiency of nitric oxide, but one would expect that in the presence of added nitric oxide the number of moles of methane not appearing would equal the number of moles of nitromethane prevented from reacting. It was found, however, that the reduction in the number of moles of methane corresponds to only 10% of the number of moles of nitromethane not reacting. It has been observed in all the high-pressure experiments, even in the absence of added nitric oxide, that the concentration of methane among the decomposition products is much lower than had been reported for the low-pressure studies. If the mechanism proposed by Cottrell is applicable at high pressures, it must be assumed that methane is removed by reaction with other compounds that are present. The most likely one is nitrogen dioxide, but the reaction of methane and nitrogen dioxide yields nitromethane:

$$2CH_4 + 3NO_2 \longrightarrow 2CH_3NO_2 + NO + H_2O \qquad \text{Reference 4} \qquad (3)$$
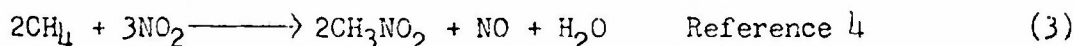
Harnsberger (Reference 4), who studied the reaction of methane and nitrogen dioxide, also reports the following reaction:

$$CH_3NO_2 + 2.5\ NO_2 \longrightarrow CO_2 + 3.5\ NO + 1.5\ H_2O \qquad (4)$$

Combining the rate laws for reactions (3) and (4), he obtains the following expression for the rate of disappearance of nitrogen dioxide:

$$-\frac{d(NO_2)}{dt} = 1.5\ k_3\ (NO_2)(CH_4) + 2.5\ k_4\ (CH_3NO_2)(NO_2)$$

where $\dfrac{k_4}{k_3} = 10$.

Considering that reaction (4) is much faster than reaction (3), and also that the concentration of nitromethane is much larger than that of methane in the experiments reported in the present investigation, one may conclude that only a relatively small amount of methane should disappear by reaction with nitrogen dioxide. It was proposed in the last report that if the reaction

$$CH_3 + NO \longrightarrow (CH_3NO) \longrightarrow HCN + H_2O \qquad (5)$$
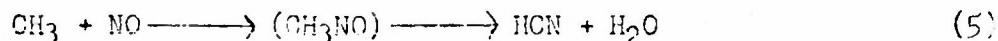
is important, an increase in the concentration of hydrogen cyanide in the presence of a large excess of nitric oxide may be expected; however, a decrease in the hydrogen cyanide concentration was observed. This may be due to experimental uncertainty, and will be checked. It may be concluded, however, that no substantial increase in the concentration of hydrogen cyanide has occurred in the presence of added nitric oxide.

       c.   All these observations support the assumption that radicals other than methyl radicals may be involved. Perhaps the initial step is that proposed by Taylor and Vesselovsky (Reference 5)

$$CH_3NO_2 \dashrightarrow CH_3NO + O \qquad (6)$$

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II Kinetic Study of the Thermal Decomposition   Report No. 717
   of Nitromethane, D (cont.)

although the energetics are difficult to explain; or the radical CH_2NO_2 may actually play a part in the decomposition of nitromethane. It is expected that the identification of all the products formed in the presence of added nitric oxide will aid in the determination of the types of radicals that are important (Section C-2-N). It is also planned to study the effects of added nitrogen dioxide and of methyl radicals on the decomposition of nitromethane.

3.   Molecular Mechanism

a.   It was pointed out (Reference 1) that nitromethane may also react in a bimolecular reaction with one or more of the decomposition products. Among these reactions the following was proposed:

$$CH_3NO_2 + HCN \longrightarrow CH_3CN + HNO_2 \tag{7}$$
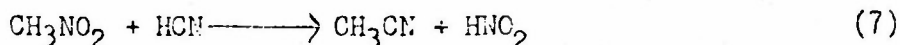
If this reaction occurs, the addition of hydrogen cyanide should increase the concentration of acetonitrile. This was found to be the case (Table IV). Reaction (7) is probably not of great importance, however, since if it were, the concentration of hydrogen cyanide during the decomposition of nitromethane alone should be considerably lower and the concentration of acetonitrile should be higher than is observed. The identification of all the products formed in the presence of added hydrogen cyanide will assist in clarifying further to what extent hydrogen cyanide influences the decomposition of nitromethane itself.

4.   Discussion of Certain Reaction Products

a.   Nitric Oxide

(1)   Some evidence had been obtained that the concentration of nitric oxide is dependent on the initial pressure of nitromethane (Reference 1). Additional experiments indicate that at the lowest pressures studied (approximately 80 psia) the nitric oxide concentration may be relatively higher, but that between 140 and 310 psia initial pressure, the concentration of nitric oxide is essentially independent of initial pressure (Table V). Further tests will be conducted to verify these analyses.

(2)   It was mentioned in the previous report that Behrens (Reference 5) had suggested that when nitric oxide reacts with carbon-containing radicals one of the products may be carbon monoxide. The mass spectrometer analyses of the reaction products from the tests with added nitric oxide show definitely that the concentration of carbon monoxide has increased. The concentration of nitrogen also increased substantially while that of carbon dioxide decreased. In general, an increase in the amount of nitrogen might be expected when a nitrogen-containing compound such as nitric oxide is added, but at present it is difficult to fit all these data into a

reaction scheme. As more is learned of the various aspects of the thermal decomposition of nitromethane, however, all these facts will be integrated into a mechanism.

III. RESEARCH ON THE PREPARATION OF NEW ROCKET PROPELLANTS

A. INTRODUCTION

Work has continued during the present report period on the improvement of the synthesis of N-aminoethylenimine. Important physical properties of the compound were also determined. Work has also begun on the synthesis of a new compound, N,N,N'-trimethyltriazane. This compound is estimated to have a specific impulse identical with that of hydrazine, while its melting point should be considerably lower.

B. SYNTHESIS OF N-AMINOETHYLENIMINE

1. Efforts to prepare N-aminoethylenimine by the dehydration of ethanolhydrazine have continued. Previous work (Reference 7) indicated that if ethanolhydrazine was esterified with sulfuric acid, and the resulting ester decomposed in aqueous base, the product obtained always showed acetaldehyde, hydrazine, and high-boiling materials on analysis. It was found also that these impurities were formed during the ring-closing step, i.e., in the treatment of the ester with aqueous base. As a possible means of avoiding these side reactions the ester was decomposed in an ethylene glycol solution of sodium hydroxide. The results of several experiments indicated that if the decomposition was carried out at reduced pressure (25 to 100 mm) and at about 135°C, the yield of crude product (35%) was approximately the same as when aqueous base was used, but that neither acetaldehyde nor hydrazine was present in the crude material. However, the crude product was still contaminated with higher-boiling materials. In working up the product, the distillate from the decomposition of the ester was fractionated, affording a cut boiling over the range of 53 to 58°C at 100 mm pressure. This apparently consisted of N-aminoethylenimine and water formed during the decomposition reaction. Sodium hydroxide pellets were added to this mixture and an oil was easily separated. The volume of the organic layer was usually about one-third that of the aqueous layer. An analysis of the pot residue, by titration with potassium iodate, indicated that about forty per cent of the reducing function had not distilled. Apparently higher-boiling substances than N-aminoethylenimine had formed, or an azeotrope exists between N-amino-ethylenimine and ethylene glycol. Because of the presence of side reactions in the decomposition of the ester, it is desirable to carry out this step of the synthesis at as low a temperature as possible. This might be accomplished through the use of a stronger base than sodium hydroxide. Work is now in progress to determine the effect of sodium methylate in ethylene glycol as the reaction medium.

2.   In order to obtain a sufficient quantity of pure N-amino-ethylenimine to determine adequately its physical properties, the decomposition of the ester was scaled up tenfold. The yield of crude product dropped to about fifteen percent. This situation apparently arises through the addition of the ester to a reaction medium which becomes progressively more contaminated with products from side reactions, and which react destructively with the N-aminoethylenimine.

3.   Probably the most economically attractive method for preparing N-aminoethylenimine is the nitrosation of ethylenimine and subsequent reduction. Previous attempts (Reference 8) to nitrosate ethylenimine were unsuccessful, but the reactions were carried out in aqueous media in which ethylenimine might be expected to polymerize readily. Consequently, two further attempts were made to carry out this reaction. Ethanolic ethyl nitrite was added dropwise at 0°C to an ethanol solution of stoichiometric amounts of ethylenimine and acetic acid. The mixture was permitted to stand for two days at room temperature, and was then distilled. Ethyl nitrite and acetic acid were partially (about 50%) recovered. The ethylenimine polymerized and remained as a tarry residue in the distillation pot. In another experiment the considerably less polar n-butyl ether was used as the solvent, and isoamyl nitrite was employed as the nitrosating agent. Isoamyl nitrite was chosen so that the reaction could be carried out, if desired, at a higher temperature than if ethyl nitrite had been used. Anomalous results were obtained in this experiment, since on distillation almost all of the material boiled below 60°C. This experiment will be repeated, but acetyl chloride will be added as an acidic catalyst for the reaction.

C.   PHYSICAL PROPERTIES OF N-AMINOETHYLENIMINE

     A sample of crude N-aminoethylenimine was distilled in a highly efficient column. The fraction boiling at 72 to 74°C at 475 mm was collected as pure N-aminoethylenimine. The following physical properties of the material were determined:

bp_{746}	82.0°C
mp	−65 to −59°C
d^{23}	0.906
η^{23}	0.973 centistokes
ΔH_c	431 kcal/mole

D.   SYNTHESIS OF N,N,N'-TRIETHYLTRIAZANE

1.   The alkyl triazanes as a class are unknown. A few highly substituted aryltriazanes are known (Reference 9); these are high-melting solids. An indication that the simple alkyltriazanes should be liquids with low melting points is to be found in the observed physical properties of the nitrosoalkylhydrazines. Nitrosomethylhydrazine melts at $45^\circ C$, while nitroso-sym-dimethylhydrazine and dinitroso-sym-dimethylhydrazine are liquids at room temperature (Reference 10). The reduced compounds (triazanes) should melt at lower temperatures than their corresponding nitroso analogs.[*] In particular, nitrosotrimethylhydrazine, which has recently been prepared in this laboratory, melts at $-7^\circ C$ and should afford a reduction product melting at a considerably lower temperature.

2.   The following reaction sequence was employed in attempting the synthesis of N,N,N'-trimethyltriazane:
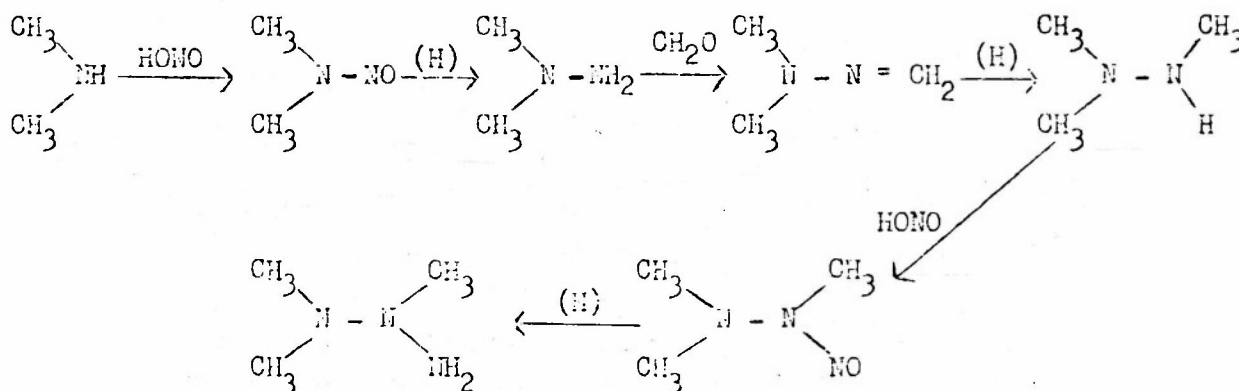
3.   Unsym-dimethylhydrazine was synthesized from dimethylamine essentially according to the method of Hatt (Reference 11). A concentrated aqueous solution of the base was used for the subsequent reaction.

4.   Methylenedimethylhydrazine was prepared through the addition of forty percent aqueous formaldehyde to aqueous unsym-dimethyl-hydrazine, as described by Aston (Reference 12). The product was salted out with sodium hydroxide pellets, and distilled from solid sodium hydroxide. The yield of product, bp 69 to $70^\circ C$, was about 95 percent.

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[*] For example, nitrosodimethylamine melts at $-29^\circ C$; its reduction product, unsym-dimethylhydrazine, melts at $-51^\circ C$.

III Research on the Preparation of New Rocket
Propellants, B (cont.)

Report No. 717

5.   Trimethylhydrazine was prepared by the lithium aluminum
hydride reduction of methylenedimethylhydrazine, as described by Aston
(Reference 7). The product was isolated by separation as the hydrochloride,
followed by distillation from excess sodium hydroxide after neutralization.
The yield of product, bp 59°C, was about 45 percent. A potentiometric
analysis with potassium iodate indicated a purity of 94.4 percent; the
residual material was presumably water.

6.   Trimethylhydrazine was converted to the nitroso derivative
essentially according to the method of Thiele (Reference 13). An aqueous
solution of the base was carefully treated with acetic acid to a pH of 5.5
in the presence of a 2-mole excess of sodium nitrite. On standing overnight
the solution gradually became neutral (pH = 6.90). The solution was then
extracted continuously with ether until all of the yellow color had passed
into the ether layer. The ether solution was dried over anhydrous magnesium
sulfate, the ether was removed, and the residue was distilled at reduced
pressure. The yield of product boiling at 43°C at 10 mm pressure was about
50 percent. This compound, which has not previously been prepared, is a
light-yellow oil melting at -7°C. Its aqueous solution is neutral, and
it hydrolyzes immediately in 6N hydrochloric acid at room temperature. It
gives a positive Liebermann test for the nitroso group. The compound is
stable at dry-ice temperatures, but at room temperature it slowly decomposes.
A sample at room temperature becomes orange-yellow in about three days, and
orange-brown in a week. A sample of the material was submitted for an
analysis of carbon, hydrogen, and nitrogen, but the results are not yet
available.

7.   The reduction of nitrosotrimethylhydrazine has been carried
out on a small scale. When 0.7 g of the nitroso compound was hydrogenated
in the presence of 0.7 g of 10 percent palladium on charcoal in 45 ml of
water at 29°C and atmospheric pressure, 75 percent[*] of the theoretical two
moles of hydrogen per mole of nitroso compound was absorbed in 2 hr. The
rate of hydrogenation was constant until about 1.2 moles were absorbed, when
the rate decreased gradually, and finally became zero at 1.5 moles. The
catalyst was filtered off, and a portion of the sample was titrated with
potassium iodate. The results indicated that if N,N,N'-trimethyltriazane
were the only reducing substance present, and if this compound undergoes a
four-electron change during oxidation, the yield of the desired product was
about 65 percent. No further work was done on this small quantity of
material. Further reductions of nitrosotrimethylhydrazine are planned;
hydrogen, in the presence of palladium on charcoal, lithium aluminum hydride,
and sodium amalgam in ethanol will be employed as reducing agents.

8.   The course of the reduction of the above-described sample
of nitrosotrimethylhydrazine can be predicted to some extent. Since the

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[*]Impurities in the nitroso compound due to decomposition before the hydro-
genation could account for the discrepancy in hydrogen uptake.

III Research on the Preparation of New Rocket   Report No. 717
    Propellants, D (cont.)

final reaction mixture contained a function titratable by potassium iodate,
cleavage could not have occurred at the hydrazine bond:

$$CH_3\diagdown N - N - NO \xrightarrow{(H)} CH_3\diagdown NH + CH_3NHNO$$

$$\diagdown CH_2H_2 + H_2O \qquad CH_3OH + H_2$$
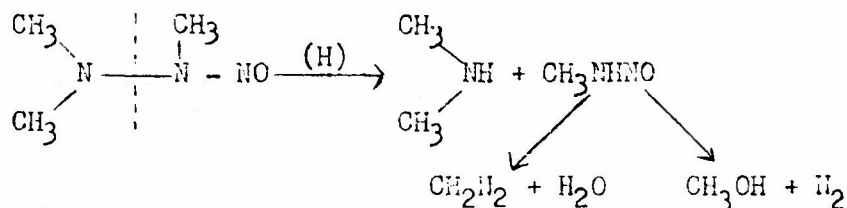
However, cleavage at the remaining N-N bond could form trimethylhydrazine,
oxidizable by potassium iodate:

$$CH_3 - N - N - NO \xrightarrow{(H)} CH_3 - N - N + (NOH)$$

$$2(NOH) \longrightarrow H_2N_2O_2$$
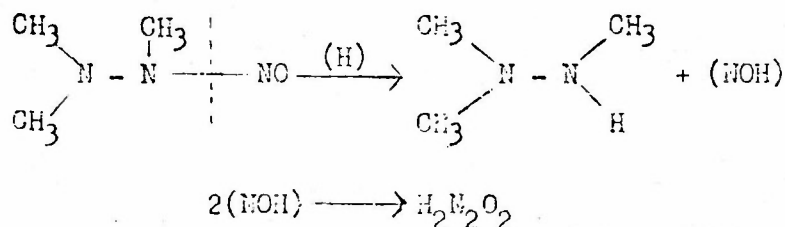
The hyponitrous acid would presumably undergo further reduction to account
for the absorption of additional hydrogen. Another possible reaction course
is as follows:

$$CH_3 - N - N - NO \xrightarrow{(H)} CH_3 - N - N - NHOH \xrightarrow{(H)} CH_3 - N - N + NH_2OH$$
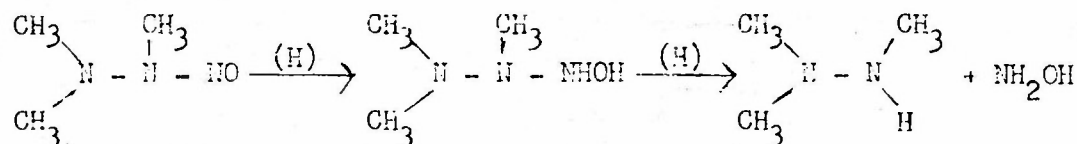
Clearly, additional work is required to determine the course of the reduction.

IV.   SENSITIVITY OF METHYLACETYLENE

    A.   The sensitivity of liquid methylacetylene to rapid compression
has been determined in the presence of oxygen, nitrogen, and vapor alone, at
32°F and at 165°F. The frequency of detonations is appreciable even at
pressurization rates below 20,000 psi/sec. It is larger with oxygen or
nitrogen than with vapor alone, and it is larger at 165°F than at 32°F.
Detonation is no more likely with oxygen than with nitrogen.

B.   No detonations were observed when the liquid, without a gas or vapor space, was expelled through sharp-edged orifices at pressure drops up to 20,000 psi.

C.   The vapor pressure of methylacetylene was measured from ambient temperature to near 165°F. The experimental data agreed closely with the extrapolations of the low-temperature data.

D.   Complete details of the testing of methylacetylene are presented in Reference 14.

E.   It is considered that methylacetylene would exhibit marginal safety in rocket engine applications because of the appreciable detonation frequency at pressurization rates below 20,000 psi/sec; the material should therefore be used with adequate precautions.

V. ENGINE TEST PROGRAM

Because of the necessity of completing the determination of the sensitivity of methylacetylene, it was not possible to operate the 100-lb-thrust rocket motor, which is housed in the same test facility, during this report period. The motor system has now been thoroughly cleaned and dried, however, and the instrumentation has been calibrated in preparation for testing aviation gasoline with mixtures of fluorine and oxygen. Testing is expected to begin during the first week of June. The first tests will be made with 100% oxygen in order to establish a standard for future comparison with the fluorine mixtures.

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TABLE I

THERMAL DECOMPOSITION OF NITROMETHANE

Rate Constants for 1.3-Order Reaction

Temperature: 355°C

Duration: 31 min

Run No.	Initial Pressure of Nitromethane psia	$k_{1.3\text{-order}}$ $cc^{0.3}\,mole^{-0.3}\,min^{-1}$
83	75.7	0.14
78	82.2	0.14
113	85.4	0.15
72	92.3	0.12
71	144.9	0.12
62	162.4	0.14
67	177.3	0.12
55	188.3	0.15
106	183.9	0.13
65	233.6	0.11
58	246.5	0.13
80	258.4	0.14
93	260.1	0.14
64	263.1	0.10
105	273.3	0.13
66	283.0	0.12
61	293.1	0.12
60	221.2	0.12
59	365.6	0.13

Table I

TABLE II

THERMAL DECOMPOSITION OF NITROMETHANE

Effect of Additives

Temperature: 355°C

Duration: 31 min

Run No.	Additive		Initial Pressure of Nitromethane, psia	% Decomposed
	Type	%		
75	NO	0.93	289	29.5
94	NO	1.0	275	28.5
99	NO	18.9	274	14.8
101	NO	20.8	264	18.4
111	CO_2	20.7	165.9	28.1
108	CO_2	17.7	177.9	28.5
*	None	--	270	28.8
*	None	--	170	26.2

*Values taken from Figure 1.

Table II

TABLE III

NITROMETHANE DECOMPOSITION PRODUCTS[*]

Effect of Nitric Oxide

Temperature: 355°C

Duration: 31 min

Run No.	Initial Pressure of Nitromethane psia	% NO added	% Products Formed				
			CO_2	N_2O	N_2	CO	CH_4
107	144	19.8	33.6	4.9	29.7	29.9	1.7
101	264	20.8	18.2	3.1	37.6	41.1	0
99	274	18.9	20.3	1.8	37.3	40.6	0
113	85	0	31.4	12.2	20.1	22.4	13.9
114	202	0	39.6	11.6	19.9	19.3	9.6
92	310	0	51.1	4.3	17.2	19.6	7.8

[*]All products completely volatile at -78°C under the experimental conditions are included, except nitric oxide.

Table III

TABLE IV

NITROMETHANE DECOMPOSITION PRODUCTS

Effect of Added Hydrogen Cyanide

Temperature: 355°C

Duration: 31 min

Run No.	Initial Pressure of Nitromethane psia	% HCN added	CH_3CN	NO	N_2	CO	CH_4	CO_2	N_2O
103	254	21.0	11.1	30.4	13.0	12.1	4.9	25.1	3.2
92	310	0	4.5	28.7	11.5	13.1	5.2	34.1	2.9

Table IV

TABLE V

NITROMETHANE DECOMPOSITION PRODUCTS

Effect of Initial Pressure

Temperature: 355°C

Duration: 31 min

	Run 78	Run 113	Run 32	Run 114	Run 68	Run 92
Initial Pressure (psia)	82	85	194	202	292	310
Constituent*			Composition, Mole %			
N_2O	0.7	7.5	--	8.2	--	3.0
NO	47.6	38.4	18.3	29.0	33.3	30.1
N_2	9.2	12.4	22.7	14.1	12.8	12.1
CO_2	25.2	19.4	45.4	28.1	38.5	35.7
CO	11.6	13.8	13.6	13.7	15.4	13.7
CH_4	5.7	8.6		6.8		5.5

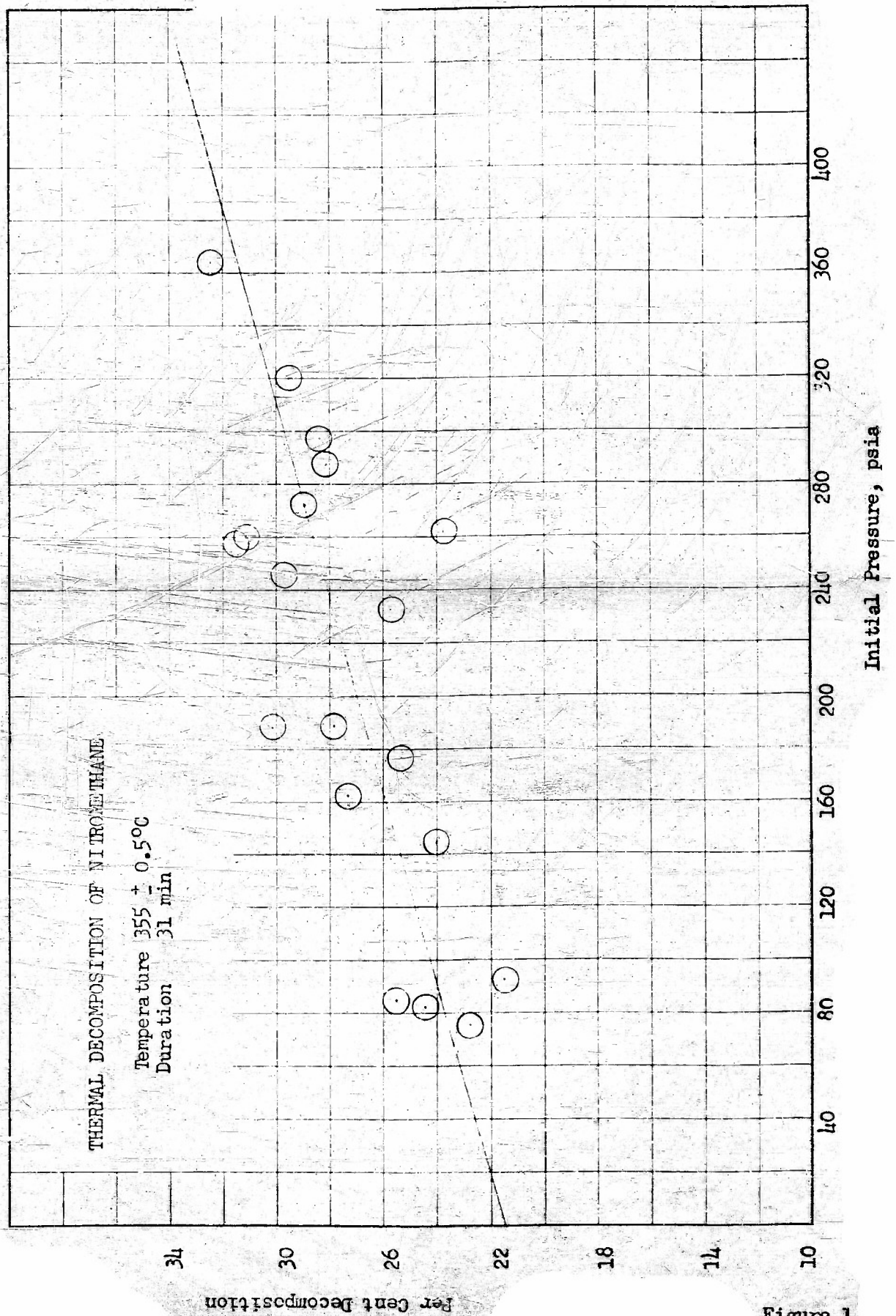*Only products completely volatile at -78°C under the experimental conditions are included.

Table V

THERMAL DECOMPOSITION OF NITROMETHANE

Temperature 355 ± 0.5°C
Duration 31 min

C-3407   KHM

Initial Pressure, psia

Per Cent Decomposition

Figure 1